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(19)(CA) APPLICATION FOR CANADIAN PATENT (12)

(54) Dispersion of Polysiloxane, a Method for Its Production and Its Use

(72) Pyrlik, Manfred - Germany (Federal Republic of) ;
Block, Hermann - Germany (Federal Republic of) ;

(73) Hanse Chemie G.m.b.H. - Germany (Federal Republic of) ;

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Abstract

The invention deals with a polysiloxane dispersion with a 25 to 00.3% by weight outer phase consisting of monomeric or polymeric polyoles liquefying at temperatures of 20 to 100°C, linear or ramified polyglycolethers, polyesters on a polyole base, and aliphatic, cycloaliphatic or aromatic dicarboxylic acids, aliphatic polylactones and/or polycarbonates, 0.1 to 75% by weight of a dispersed phase consisting of one or several three-dimensionally polymerizable polyorganosiloxanes, the polymerized polyorganosiloxane particles having a mean diameter of 0.02 to 50 µm, and 0 to 20% by weight solvents, softeners, polymerizers, catalysts, stabilizers, dispersants, hardeners, reaction-mediators, and/or agents to influence the viscosity of the outer phase.

The invention further deals with a process for the production of these polysiloxane dispersions and their use as preliminary products for the production of silicon-modified thermoplastic, duroplastic or elastomeric plastics on a polyurethane, polyurea, saturated polyester and polycarbonate base.

Polysiloxane dispersion, process for its production and use

The invention deals with a polysiloxane dispersion, a process for its production and its use as an intermediate product in the production of silicon-modified thermoplastic, duroplastic or elastomer plastics.

Combination products of polyorganosyloxanes with organic carbon compounds, for example polyoles, polyethers and polyesters, are already known. These, however, as a rule are copolymers wherein polysiloxane chains are linked to the organic carbon polymer according to the main valence. Such products have been dascribed in the monograph "Chemistry and technology of silicones" by W. Noll, Weinheim/Bergstrasse 1999968, p 317 ff. Copolymers consisting of dioles and polyoles with polyorganosiloxanes are alsc known from DE-A-25 12 632. Polysiloxanoles are obtained that are recommended for the modification of urethane or epoxy resins. It has been found, however, that with this type of modification the polysiloxanes

are dispersed homogeneously, that is with molecular dispersion, in the polymer, which is often detrimental to the mechanical strength and chemical stability of the resulting plastics. Combinations of polyorganosiloxanes with polyethers or polyesters are also known, that form systems wherein the polyorganosiloxane components form the outer phase and the organic carbon components the dispersed phase. Thus organic multicomponent dispersions are known from EP-A-0058340 that consist of polyorganosiloxane-polyether-polyester-cork copolymers as dispersed phase and polyorganosiloxanes as outer phase. These are thus modified polyorganosiloxanes and not polyether or polyester modified by polyorganosiloxane.

A filler material has been described in EP-A-0304946 consisting of finely dispersed silicon rubber with a particle diameter of 1 mm or less, produced in water by dispersion of a hardenable silicon rubber protective compound containing a specific silane or its products of partial hydrolysis in free form or chemically bound to the silicon rubber. Silane has an unsaturated alkenyl radical in the terminal position, optionally with a functional group such as an epoxy, amino, acryloxy, methacryloxy or mercapto group. This filler material should be used as admixture to improve the physical qualities of organic resins and synthetic rubbers.

Finally, suspensions are known as outer phase from DE-A-36 34 084, with elastomeric polyorganosiloxane as dispersed phase and reaction resins that can be processed into duroplasts, used

for example as intermediate products in the production of duroplastic masses, insulating materials and molded laminated plastics.

The task of this invention is to produce suitable silicon-containing intermediate products that are readily compatible with various types of plastics, can be processed easily and offer various possible applications, so that diverse silicon-modified plastics can be produced with their aid, thermoplastic as well as duroplastic and elastomeric plastics that have improved physical and chemical qualities. The desired qualities of silicones, such as heat stability, will be maintained in the resulting plastics, while undesirable qualities of silicones, such as low mechanical strength, should not remain as far as possible in the silicon-modified plastics. At the same time the characteristic physical and chemical qualities of the plastics to be modified should not be affected, or as little as possible.

In this invention the task is solved by polysiloxane dispersion, characterized by containing

(a) 25 to 99.9% by weight of an outer phase consisting of monomeric or polymeric polyoles that liquefy at temperatures of 20 to 100°C, linear or ramified polyglycolethers, polyesters on a polyole base, and aliphatic cycloaliphatic or aromatic dicarboxylic acids, aliphatic polylactones and/or polycarbonates,

(b) 0.1 to 75% by weight of a dispersed phase consisting of one or several three-dimensionally polymerizable

polyorganosiloxanes, the polymerized polyorganosiloxane particles having an average diameter of 0.02 to 50μm, and

(c) 0 to 20% by weight of known accessory materials, such as solvents, softeners, polymerizers, catalysts, stabilizers, dispersants, hardeners, reaction-mediators and/or agents to influence the viscosity of the outer phase.

It was found surprisingly that the proposed specifically designed polysiloxane dispersion of this invention could be used as intermediate product for very many purposes, for it has excellent compatibility with many types of plastics and endows the plastics with the desirable qualities of silicones, without appreciably affecting the inherent desirable physical and chemical qualities of these plastics. Thus with the polysiloxane dispersion of this invention it is possible to produce silicon-modified thermoplastic, duroplastic or elastomeric plastics with a combination of properties that is valuable in practical applications and excellent workability, as will be described in detail below.

For the purposes of this invention a number of known compounds may be used as monomeric polyoles. Because of the ready availability and advantages, particularly the excellent compatibility and workability of the resulting products, use is made as polyoles for the outer phase of the dispersion of this invention preferably of linear or ramified aliphatic glycols, the outer phase of the polysiloxane dispersion consisting preferably of ethylene glycol, 1,2- or 1,3-propanediol, 1,2- or 1,4-

butanediol, 1,6-hexanediol, 2,2,4-trimethylpentadiol-1,3, and/or neopentylglycol.

Additionally glycerine, trimethylolpropane or sugar alcohols, particularly erythrite, xylite, mannite and/or sorbite may preferably be used as aliphatic polyoles. The outer phase may use as preferred polyoles one or several alicyclic polyoles, particularly 1,4-cyclohexanedimethanol, and/or saccharose.

Possible polymeric polyoles for the outer phase may preferably be those having an average molecular weight of 200 to 2,000, the polymeric polyole being preferably one with a (meth)acrylic acid alkylene glycol ester base. The outer phase of the dispersion of this invention may also advantageously have polymeric polyoles that are obtained by saponification or partial saponification of vinyl ester-containing polymers.

Possible polyethers for the outer phase may be above all linear or ramified polyglycolethers obtainable by ring-opening polymerization of cyclic ethers in the presence of polyoles, for example the polyoles referred to above, among which preference is given, because of the relative availability, to polyethylene glycol, polypropylene glycol and/or polytetramethylene glycol or their copolymers.

Possible polyesters for the outer phase of the dispersion of this invention are those having a polyole base and aliphatic, cycloaliphatic or aromatic dicarboxylic acids, notably all appropriate saturated polyesters that liquefy at temperatures of 20 to 100°C, preferably succinic acid ester, glutaric acid ester,

adipinic acid ester, phthalic acid ester, isophthalic acid ester, terephthalic acid ester, and/or the esters of the appropriate hydration products, the alcohol components consisting of monomeric or polymeric polyoles, for example those of the type referred to above.

Other polyesters that may be used in this invention are aliphatic polylactones, preferably ε-polycaprolactone, and/or polycarbonates, accessible for example by polycondensation of diols with phosgene. For the outer phase, polycarboxylic acid esters of bisphenol-A may be used that have an average molecular weight of 500 to 100,000.

Instead of the above polyoles, polyethers and saturated polyesters, use can be made for the purposes of this invention of mixtures of the above classes of substances for the outer phase of the polysiloxane dispersion of this invention. The use of such mixtures may be advantageous by reducing the hardening or melting temperatures of the resulting products.

To influence the viscosity of the outer phase, particularly to reduce viscosity or for liquefaction, there may optionally be added to the polyoles, polyethers and saturated polyesters or their mixture for the outer phase of this invention additional appropriate accessory substances, particularly solvents, softeners, diluents and the like.

The dispersed phase of the polysiloxane dispersion of this invention consists of one or several three-dimensionally polymerizable polyorganosiloxanes, the polyorganosiloxane

particles dispersed in the outer phase having a mean diameter after polymerization of 0.02 to 50 µm preferably 0.05 to 10 µm, even more preferably 0.07 to 5 µm and most preferably 0.07 to 1 µm. These polyorganosiloxane particles have reactive groups on their surface through which they can be chemically bound to the components of the outer phase, namely to the monomeric or polymeric polyoles, polyglycolethers and/or polyesters used.

Among the many three-dimensionally polymerizable polyorganosiloxanes those are used for preference that are derived from siloxane units with the general formula

$$-(R_2SiO)- \qquad (1)$$

wherein the two monovalent radicals R that my be identical or different contain linear or ramified alkyl groups with 1 to 19 C-atoms, cycloaliphatic groups with 4 to 8 C-atoms, linear or ramified alkenyl groups with 2 to 4 C-atoms, phenyl or alkylphenyl groups with 1 to 12 C-atoms in the aliphatic radical, wherein the hydrocarbon radicals may also be substituted with halogens or hydroxyl, carboxyl, carboxylic acid anhydride, amino, epoxy, alkoxy or alkenyl-oxy groups, representing polyether or polyolefin groups or hydrogens, the groups being bound directly or via an oxygen or nitrogen atom to a silicon atom of the polysiloxane chain.

Examples of such R radicals are methyl, ethyl, isopropyl, isobutyl, dodecyl, and octadecyl groups, cyclopentyl, cyclohexyl and cyclooctyl groups, vinyl, allyl, isopropenyl and 3-butenyl

groups, ethylphenyl, dodecyl groups, as well as groups with hydrocarbon radicals that may in part be substituted for instance with halogens, particularly fluorine, chlorine, as for instance the chloropropyl or 1,1,1-trifluoropropyl radical. At least some of the R radicals may also consist of polymeric groups, possibly polyethers such as polyethylene, polypropylene, polybutylene or polyhexamethylene glycol or polytetrahydrofurane, and mixed polymers of these ethers, as well as polyolefins, for instance polybutadiene, polyisoprene, polybutene, polyisobutene, and the like. Finally some of the R radicals may also be hydrogen. It is also possible to use mixtures of the above polyorganosiloxanes.

According to the invention it is also possible without difficulty to use polyorganosiloxanes wherein various R radicals are present in the polymer molecule. These various radicals may also be statistically dispersed alongside the main siloxane chain. In a preferred version, the polyorganosiloxane used according to this invention may be a block co-polymer wherein monovalent R′ and R′′ radicals are arranged in blocks alongside the main siloxane chain, derived from polymeric units with the general formula

$$-(R'_2SiO)_x-(R''_2SiO)_y- \qquad (2)$$

wherein the R′ and R′′ radicals that have the same significance as R differ from one another while the R′ and R′′ radicals may be identical or different, and x and y are equal to 1 or whole

multiples thereof.

Because of their ready availability and good effectiveness, those polyorganosiloxanes are preferred wherein at least 50% of the R, R' or R'' radicals represent methyl and/or phenyl groups.

The invention further deals with a process for the production of polysiloxane dispersions according to claims 1 to 19, wherein

a) an emulsion consisting of 0.1 to 75% by weight of one or several three-dimensionally polymerizable liquid polyorganosiloxanes is used as dispersed phase in 25 to 99.9% by weight of an outer phase consisting of monomeric or polymeric polyoles liquefying at temperatures of 20 to 100°C, linear or ramified polyglycol ethers, polyesters on a polyole base, and aliphatic, cycloaliphatic or aromatic dicarboxylic acids, aliphatic polylactone and/or polycarbonates, and produced with 0 to 20% by weight of known accessory substances, particularly solvents, softeners, polymerizers, catalysts, stabilizers, dispersants, hardeners, reaction-mediators and/or agents to influence the viscosity of the outer phase, wherein the polyorganosiloxane droplets are present with an average diameters of around 0.01 to 5 µm, and

b) polymerization takes place in the droplets of polyorganosiloxane by a known process, forming solid particles.

In step a) preferably 2 to 50% by weight of one or several three-dimensionally polymerizable liquid polyorganosiloxanes are

used.

The mean molecular weight of the liquid polymerizable polyorganosiloxane that can be used in this invention may vary within broad limits and is generally between 800 to 500,000. The lower limit is determined by the fact that with decreasing molecular weight the density of polymerization of polyorganosiloxanes increases and thereby its elasticity decreases. This effect, however, can be reduced within certain limits by the addition of bifunctional polymerizers. The upper limit is determined by the viscosity of the polyorganosiloxanes which increases with rising molecular weight, impeding the desired fine dispersion in the liquid outer phase. Therefore in step a) preferably these polymerizable polyorganosiloxanes or polyorganosiloxane mixtures are used that have a mean molecular weight of 1,000 to 100,000, particularly one of 1200 to 30,000.

In the dispersion of this invention the particle size of the polymerized polyorganosiloxanes may vary within broad limits according to the profile of qualities aimed at by modification. Since with increasing average particle size the effectiveness of the polyorganosiloxane modification becomes progressively lower, for economic considerations a mean particle diameter of a maximum of 50 µm is expedient. On the other hand both the workability and the long-term stability of the dispersions of this invention are reduced with decreasing particle size, so that it has not proved to be useful to use a particle diameter of less than 0.02 µm. Accordingly, in the process of this invention the

polymerizable liquid polyorganosiloxanes are so finely dispersed in the outer phase that the polysiloxane particles formed have a mean diameter of around 0.02 to 50 µm, preferably of around 0.05 to 10 µm, even more preferably of around 0.07 to 5 µm and most preferably of around 0.07 to 1 µm.

The distribution of particle size as a rule is not critical and may include for instance the preferred or the particularly preferred range, either entirely or in part. However, in many cases it may be expedient, in order to achieve certain qualities, to select a more or less narrow distribution of particles. To achieve special effects, a bi or trimodal distribution may also be used.

The concentration of polymerizable polyorganosiloxanes in the dispersion of this invention depends largely on the nature of the effect :ended through modification and upon the particle size of the polyorganosiloxane. Thus in some cases even relatively small quantities of polymerizable polysiloxanes, down to 0.1% by weight in the dispersions of this invention, may be sufficient, while the upper limit is determined by the stability of the dispersion and the maximum filling of space by the outer phase, and according to this density, amounts to a maximum of 75% by weight.

The process of this invention may be carried out in various forms. A preferred form consists of dispersing the liquid polymerizable polyorganosiloxane in an initial liquid medium which is miscible with the actual outer phase, and the

dispersion obtained is added to the actual outer phase and mixed therewith, and polymerization of the polyorganosiloxane takes place in an appropriate manner, before, during or after mixing with the actual outer phase, and optionally the first dispersion medium may be removed after termination of mixing.

Only those liquids can be considered to be a first dispersion medium whose presence in the end product is desirable or at least not detrimental, as for instance solvents with relatively low boiling points, relative diluents or softeners, but preferably water.

In an other equally preferred version of the process of this invention the polymerizable liquid polyorganosiloxanes are first dispersed in an initial liquid medium which is not miscible with the actual outer phase, whereupon the dispersion obtained is mixed with the actual outer phase, after which the first dispersion medium is removed entirely or in part by appropriate means, and polymerization of the polyorganosiloxanes is carried out before, during or after mixing with the actual outer phase or separation of the first medium.

In this version of the process those liquids are a possible first dispersion medium that can be removed by appropriate means, for example by distillation, after mixing with the polyoles, polyethers and polyesters to be modified according to the invention, or mixtures thereof, without affecting the desired qualities. Solvents with a low boiling point, or preferably water are suitable for this.

The dispersal of liquid polyorganosiloxanes in the outer phase can be achieved by measures known in the production of emulsions and accessory substances, for example by placing one of the two phases together with an appropriate stabilizer and adding the other phase. Emulsification takes place with the help of mechanical aggregates that exert a sufficiently strong shearing effect in the medium to be dispersed, for instance stirring devices, mixers, kneaders, dissolvers, high-pressure or ultrasound homogenizers and the like. It is also possible first to produce a coarse preliminary emulsion of polyorganosiloxane, which is then further processed in a homogenizing or fine emulsifying step, for instance with one of the aggregates referred to above, into an emulsion with the desired distribution of droplet size.

If the polyorganosiloxane to be emulsified does not have self-emulsifying properties, it is necessary to add certain dispersing agents. As a rule self-emulsification does not take place if the organo groups of the polyorganosiloxane are methyl, ethyl, vinyl or phenyl groups. On the other hand self-emulsification may be expected if at least in some of the polyorganosiloxanes used according to this invention the organo groups are longer chain polyether, polyester or aliphatic hydrocarbon radicals.

Use can be made as stabilizers of anionic, cationic or non-ionogenic emulsifiers and tensides known from the production of silicon emulsions. Their selection will naturally be determined

by the outer phase in which the polyorganosiloxanes are to be emulsified, and can be made by the expert after a few orientating preliminary experiments. To obtain particularly stable emulsions, combinations of various stabilizers may be used.

As was mentioned above, the average particle size and distribution of particle size of polyorganosiloxane particles has a distinct influence on the effectiveness of polyorganosiloxane modification and workability, as well as on the long-term stability of the dispersions of this invention. It is therefore important to be able to regulate the particle size and distribution of the particles in the dispersions of this invention, in the desired and necessary manner. This can take place in a known fashion, for example by selection and concentration of the stabilizer or stabilizers. In order to obtain the desired fine-particled emulsions, especially effective emulsifiers will be used in higher concentrations, for example in a quantity of 20 to 100% by weight, as a function of the quantity of polyorganosiloxane. A further possibility for regulating particle size or the distribution of particle size is to vary the mechanical energy used in the process of emulsification, for it is known that the mean particle size decreases with rising emulsifying energy. The particle size or particle size distribution of polyorganosiloxane particles found to be advantageous for the purposes of this invention can thus be obtained by specific variation of the conditions of emulsification and/or selection and concentration of the

stabilizers. If the object is to obtain a di, tri or multimodal distribution of particle size, this can be obtained for instance by mixing various unimodally dispersed emulsions or suspensions.

The temperature at which emulsification takes place is not critical and as a rule will be determined by the polyoles, polyethers and polyesters used, or their mixtures. If possible, for reasons of energy saving, the process of emulsification should take place at room temperature or slightly above, but it could be that with a high viscosity of the outer phase used, emulsification would have to be carried out at higher temperatures, for example up to 150°C.

Once the process of emulsification has taken place, in step b) of the process of this invention polymerization into polyorganosiloxane droplets takes place in a known manner, with formation of solid particles.

The manner or mechanism by which the liquid polyorganosiloxanes are polymerized is not critical, provided care is taken that the polymerization reaction does not appreciably disturb the fine dispersion of the polysiloxane particles and that no polymerization reactions, or only negligible ones, take place in the outer phase. Under these conditions the expert has access to a large number of different possibilities for the polymerization of polyorganosiloxanes, such as are to be found, for instance, in the monograph already cited, "Chemistry and Technology of Silicones".

In a preferred version of the process of this invention the

liquid polymerizable polyorganosiloxanes are first mixed with polymerizers and/or catalysts and only then emulsified in the outer phase, the conditions being so selected that the transition of the polysiloxane particles from the liquid to the solid state only takes place after the process of emulsification is ended.

In another equally preferred version of the process of this invention, only after the formation of the polyorganosiloxane emulsion are appropriate polymerizers and/or catalysts added, which bring about the polymerization of the liquid polyorganosiloxane particles.

Polymerization of the polysiloxane particles into solid particles can take place in particular by known processes of addition and condensation. If polymerizable liquid polyorganosiloxanes are used that polymerize by the mechanism of addition, as a rule the polymerizers used will be polyorganohydrogensiloxanes that contain a sufficient number of Si-H bonds, for example polymethylhydrogensiloxane, and as catalysts precious metals of the VIIIth secondary group of the periodic table of elements or their compounds are added. Addition polymerization usually takes place at elevated temperatures, for example between 60 and 140°C, in the presence of a precious metal catalyst.

If polymerizable liquid polyorganosiloxanes are used that polymerize by the mechanism of condensation, silanes may for example be used as polymerizers with hydrolyzable SiO or SiN bonds. Such polymerizers are for example methyl

triacetoxysilane, methyltrimethoxysilane, tetra-ethoxysilane, methyl-tris(butanonoxomino)silane, methyl-tris(cyclohexylamino)silane and the like. However, compounds of other elements containing hydrolyzable groups may also be used as polymerizers, for instance tetrabutyltitanate, or polyorganohydrogensiloxanes containing Si-H bonds. If necessary, the heavy metal compounds known to be polymerizing polyorganosiloxanes by condensation may be used as catalysts, for instance tin(II)octoate or dibutyl-tin-dilaurate.

The time at which polymerization of the liquid polyorganosiloxane droplets takes place is not critical and can be so regulated that polymerization takes place at the desired time, for example directly after emulsification, or even some time thereafter, for example a few months later. This also applies to the preferred versions of the process of the invention referred to above.

As has already been mentioned, polymerization of the liquid polymerizable polyorganosiloxanes is brought about as a rule by the addition of polymerizers and/or catalysts. If the polymerizers and/or catalysts are added before emulsification, their selection must naturally be such that the polymerization reaction does not take place under the conditions prevailing during emulsification, which might hinder the process of emulsification, but only after termination of emulsification, that is at a later, predetermined time.

The time of polymerization, that is the time within which

the polysiloxane particles are virtually completely polymerized, can be adjusted by the expert by known methods. Thus the time of polymerization, in the case of condensation polymerization, can be fixed for example by selection and concentration of the catalyst, and in the case of addition polymerization, for example by addition of a temporarily acting inhibitor, for instance a short chain alkinol. By appropriate selection of the polymerizer and/or catalyst, the period of polymerization may be very long at room temperature, for example a few days or weeks. In such cases there is the possibility of mixing the liquid polymerizable polyorganosiloxane with the polymerizers and/or catalysts some time before emulsification. Polymerization is then elicited at the desired time by elevating the temperature during or after emulsification.

The polysiloxane dispersions of this invention are very well suited for the production of silicon-modified polyurethanes, polyureas, saturated polyesters and polycarbonates. They endow these polymers with excellent physical and chemical qualities, particularly a distinctly improved heat stability a very low hardening temperature (up to -100°C), a high deviation stability, very good weather resistance, very low surface tension and good electrical qualities. Furthermore the attenuating qualities of the modified polymers are distinctly improved. Thus the polysiloxane dispersion of this invention can be used advantageously as intermediate product in the production of silicon-modified thermoplastic, duroplastic or elastomeric

plastics on a polyurethane, polyurea, saturated polyester or polycarbonate base, for example for molded articles, sheeting, coating materials, grout and the like. The qualities of the polymer obtained are also distinctly improved in many cases.

The invention is explained on the basis of the examples described below without in any way limiting its scope. All parts and percentile values given are in relation to weight unless otherwise stated.

Example 1

100 parts of a commercial polypropylene glycol with a molecular weight of ca. 2000 were mixed at room temperature with 5 parts stabilizer obtained in a known manner by hydrosilylation from 70% tri-methylsilyl-end-terminal Co-equilibrate obtained from cyclic dimethyl and methylhydrogensiloxanes and 30% polypropylene glycol produced with allylalcohol as starting molecule.

surfactant.

To this mixture, while stirring at 500 min^{-1} revolutions within 1 hour, 20 parts of a mixture is allowed to flow in consisting of

80% of a hydroxyl-end-terminal polydimethylsiloxane with a viscosity of 2000 mPa.s, and

20% of a trimethylsilyl-end-terminal polymethylphenylsiloxane with a viscosity of 800 mPa.s.

A white emulsion of polyorganosiloxane in polyether was formed, which was mixed with 1 part methyl-tris-(butanonoximino)silane and 0.01 parts dibutyl-tin-dilaurate and the total mixture was

stirred again for 5 min. Examination under a light microscope showed that the dispersion obtained contained polymerized polyorganosiloxane particles with a diameter of 0.5 to 3 µm

Example 2

100 parts ethanol were mixed with 10 parts stabilizer with a composition analogous to that of example 1, with the difference that instead of the polypropylene glycolether a polyethylene glycolether was used. To the mixture obtained, heated to 50°C, 60 parts of a dimethylvinyl-end-terminal polydimethylsiloxane with a viscosity of 5000 mPa.s was added while stirring. Next the mixture obtained was treated for 5 min in an Ultra-Turrax homogenizer. The white emulsion obtained was mixed with 1 part polymethyl-hydrogensiloxane with a viscosity of 60 mPa.s and 0.6 parts of a 1% solution of hexachloroplatinic acid in ethanol and stirred for a further 5 min. After ca. 2 hours the polydimethylsiloxane particles were polymerized. The suspension obtained was next mixed with 1000 parts 1,2-propylene glycol.

Example 3.

A mixture of 50 parts neopentyl glycol, 25 parts trimethylolpropane and 25 parts polytetramethylene glycolether (molecular weight 1000) was mixed with 25 parts of the stabilizer from example 1 and heated to 70°C while stirring. Next, 50 parts of a mixture consisting of

90% hydroxyl-end-terminal polydimethylsiloxane with a viscosity of 4000 mPa.s and

10% γ-aminopropyltriethoxysilane

were added to the previous mixture and the entire mixture was treated for 5 min in an Ultra-Turrax homogenizer. The emulsion obtained in this manner was mixed with 1 part tetraethoxysilane and this mixture was stirred for 1 hour. Ten parts of the suspension obtained were mixed with 60 parts polypropylene glycol (molecular weight 2000) and 20 parts 4,4'diphenylmethane-diisocyanate, whereupon an exothermic reaction took place and the mixture hardened into a polyurethane elastomer.

A fractured surface of the elastomer obtained was examined under the scanning electron microscope after vaporizing with gold, and a distribution of particle size of the polymerized polydimethylsiloxane particles was obtained between 0.07 and 0.5 µm. The surface of the polyurethane elastomer was considerably smoother than that of a similar polyurethane without addition of polymerized polymethylsiloxane.

Example 4

100 Parts demineralized water were mixed with 10 parts of an alkylpolyethylene glycolether with 12 EO groups and a C_{12} - C_{18}-alkyl radical per molecule. To this mixture, while stirring, 60 parts of a mixture were added consisting of

96% hydroxyl-end-terminal polydimethylsiloxane with a viscosity of 2000 mPa.s,

3.9% methyltriethoxysilane, and

0.1% dibutyl-tin-dilaurate

over a period of 20 min. The resulting mixture was treated for 5 min in an Ultra-Turrax homogenizer and the emulsion obtained was

kept for 2 hours at a temperature of 70°C.

Ten parts of this suspension were mixed with 100 parts of a polyester consisting of adipinic acid and ethylene glycol with a mean molecular weight of 2000 and an OH number of 55 at a temperature of 80°C, and the water was removed by vacuum distillation. In the resulting suspension of polydimethylsiloxane particles in the polyester the distribution of particle sizes was determined under the light microscope as being in the range of 0.5 to 1 µm.

Example 5

a) 100 parts of a commercial polypropylene glycol produced with trimethylolpropane as starting molecule and having an OH-equivalent weight of 140 were mixed with 50 parts stabilizer analogous to that of example 1 with the difference that instead of polypropylene glycol a mixture was used consisting of 60 parts polypropylene glycol and 40 parts polyethylene glycol. To this mixture, while stirring, 150 parts of a mixture of

96% of a hydroxyl-end-terminal polydimethylsiloxane with a viscosity of 2000 mPa.s and

4% methyltriethoxysilane

were added and treated in an Ultra-Turrax homogenizer. 0.2 parts dibutyl-tin-dilaurate were added to the emulsion obtained, whereupon by polymerization of polysiloxane a dispersion of polyorganosiloxane elastomers was formed in the polypropylene glycol.

b) By mixing the dispersion obtained in a) with various quantities of a polypropylene glycol (molecular weight 2000), and a stoichiometric quantity of diphenylmethane-diisocyanate (MDI), polyurethane (PU) elastomers modified according to this invention were produced with various polysiloxane contents and the properties listed below were measured. For comparison, the same measurements were made on a pure polyorganosiloxane-elastomer (that is having a 100% polysiloxane content) that had the same composition as given in example 5a), and on a pure PU elastomer (that is having a 0% polysiloxane content) that contained a polypropylene glycol (molecular weight 4000) instead of the polysiloxane elastomer.

b_1) Measurement of tensile strength with a tensile-testing machine according to DIN 53504.

The results are summarized in Table 1 and show that by modification according to this invention it is possible to obtain distinct improvement of the tensile strength of the unmodified polyurethane, although the strength of pure polysiloxane elastomers is much poorer.

Table 1

Sample no.	Polysiloxane content (%)	Breaking strength (mPa)	Breaking tension (%)
1	0	2.4	290
2	14	3.7	330
3	27	5.2	370
4	38	8.7	370
5	100	0.5	230

b_2) Determination of mechanical attenuation by

measurement of the relaxation of tension after uniaxial deformation of tension.

A simple but effective method for determining mechanical attenuation of an elastomer is determination of the relaxation of tension upon constant deformation. The measurements were made on the same samples 1 to 5 (see example 5, b_1) by determining the drop in tension observed in 30 sec after producing a 100% uniaxial deformation of tension. The results are summarized in Table 2 and show a marked increase in the relaxation of tension (expressed in % of the value immediately after deformation), compared to the two unmodified elastomers (samples 1 and 5).

<u>Table 2</u>

Sample no.	Polysiloxane content (%)	Relaxation of tension (%) as a function of initial value
1	0	5
2	14	11
3	27	18
4	38	25
5	100	5

b_3) Improvement of heat stability by modification of polyorganosiloxane.

To demonstrate the improvement in heat stability of modified polymers produced with the polyorganosiloxane dispersion of this invention, samples 1 and 4 were stored for a total of 3 weeks at 150°C. After given periods the tearing expansion was measured as a measure of heat degradation.

The results are summarized in Table 3 and show that the drop in tearing expansion taking place as a result of temperature

exposure and thus of the elastomeric character of the sample was distinctly lower in the silicon-modified polyurethane than in non-modified polyurethane.

Table 1

Time of tempering	Drop in tearing expansion in % of init.value Sample 1 (0% silicon)	Sample 4 (38% silicon)
24	72	76
86	60	66
170	31	42
360	17	25
500	14	20

Example 6

Samples were produced by mixing a polypropylene glycol dispersion modified with polysiloxane having the same composition as that of example 5a with stoichiometric quantities of isophorone-diisocyanate and at various frequencies the dielectricity constants (DK), angle of loss (tan δ) and specific resistances were measured. The results of these measurements are summarized in Table 4 and show a distinct improvement, that is reduction, in the dielectricity constant and angle of loss, and the elevation of the specific resistance as a result of modification with polysiloxanes according to this invention.

Table 4 Measuring frequency 10 kHz

Sample no.	Polysiloxane content (%)	DK	tan δ	Spec. resistance x 1-6 (Ω.cm)
6	0	4.7	0.122	316
7	15	4.8	0.118	313
8	29	4.1	0.082	535
9	40	3.7	0.062	790

The same measurements were made at higher frequencies as well, up to 10 MHz. These confirmed the results shown in Table 4 without exception.

Example 7

100 parts polytetramethylene glycol (molecular weight 1000)

50 parts OH-end-terminal polydimethyl-siloxane of 10,000 mPa.s,

2 parts tetraethoxysilane and

12 parts of the stabilizer from example 1

were mixed at room temperature and treated in an Ultra-Turrax homogenizer. After standing for 2 days a dispersion of polymerized polyorganosiloxane particles was obtained in the polytetramethylene glycol.

Using this polyorganosilane dispersion based on the invention, polyurethane samples were produced as follows:

6 parts polyorganosiloxane dispersion

3 parts diphenylmethane-diisocyanate

91 parts commercial polytetramethylene glycol prepolymer with a NCO content of 7.9%, and

8 parts 1,4-butanediol

were mixed at a temperature of 60°C, poured into a form preheated to 110°C and hardened for 16 hours at 110°C. An extremely tough elastomer was obtained containing roughly 3% silicon elastomers of a hardness of 85 according to Shore A.

For purposes of comparison a polyurethane sample was produced in the same manner without the dispersion of this invention and without diphenylmethane diisocyanate.

The samples produced with the dispersion of this invention "felt" considerably smoother, that is to say they had an appreciably lower coefficient of friction. This was confirmed by measurement of the coefficient of friction (measured according to the delivery specifications no. 5306 of the Daimler Benz Company), which yielded a value of 0.39 for a non-modified sample and 0.30 for a sample modified according to the invention.

The deviation of the samples was also measured according to DIN 53516. The measurement for the non-modified sample showed a deviation of 320 mg in the non-modified sample and one of only 170 mg in the sample modified according to the invention. The sample produced with the aid of the polyorganosiloxane dispersion of the invention thus had an almost 50% better deviation constancy than the non-modified sample

Tearing strength tests and tearing expansion measurements were also made on both samples and produced identical values within the limits of accuracy of measurement.

These results show that the surface qualities of polymers modified according to the invention are distinctly improved in

comparison with unmodified polymers.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. Polysiloxane dispersion characterized by a content of

(a) 25 to 99.9% by weight outer phase consisting of monomeric 100°C, linear or ramified polyglycolethers, polyesters on a polyole base, and aliphatic, cycloaliphatic or aromatic dicarboxylic acids, aliphatic polylactones and/or polycarbonates,

(b) 0.1 to 75% by weight of a dispersed phase consisting of one or several three-dimensionally polymerizable polyorgano-siloxanes, the polymerized polyorganosiloxane particles having a mean diameter of 0.02 to 50 µm, and

(c) 0.20% by weight of known accessory substances, particularly solvents, softeners, polymerizers, catalysts, stabilizers, dispersants, hardeners, reaction-mediators and/or agents to influence the viscosity of the outer phase.

2. Polysiloxane dispersion according to claim 1, wherein the polyoles of the outer phase are linear or ramified aliphatic glycols.

3. Polysiloxane dispersion according to claim 2, wherein the glycols of the outer phase are ethylene glycol, 1,2- or 1,3-propanediol, 1,2- or 1,4-butanediol, 1,6-hexanediol, 2,2,4-trimethylpentanediol-1,3 and/or neopentyl glycol.

4. Polysiloxane dispersion according to claim 1, wherein the polyoles of the outer phase are glycerine, trimethylol-propane, sugar alcohols and/or one or several alicyclic polyoles and/or saccharose.

5. Polysiloxane dispersion according to claim 4, wherein the sugar alcohols in the outer phase are preferably erythrite, xylite, mannite and/or sorbite.

6. Polysiloxane dispersion according to claim 4, wherein the alicyclic polyole in the outer phase is preferably 1,4-cyclohexanedimethanol.

7. Polysiloxane dispersion according to claim 1, wherein there are one or several polymeric polyoles in the outer phase with a mean molecular weight of 200 to 20,000.

8. Polysiloxane dispersion according to claim 7, wherein the polymeric polyole is a polyole on a (meth-)acrylic acid alkylene glycolester base.

9. Polysiloxane dispersion according to claim 1, wherein the outer phase contains polyethylene glycol, polypropylene glycol and/or polytetramethylene glycol or their copolymers.

10. Polysiloxane dispersion according to claim 1, wherein the polyester in the outer phase is succinic acid ester, glutaric acid ester, adipinic acid ester, phthalic acid ester, isophthalic acid ester, terephthalic acid ester and/or the esters of the corresponding products of hydration, the alcohol component consisting of monomeric or polymeric polyoles.

11. Polysiloxane dispersion according to claim 1, wherein the outer phase contains polymeric polyoles that are obtained by saponification or partial saponification of polymers containing vinyl esters.

12. Polysiloxane dispersion according to claim 1, wherein the outer phase contains ε-polycaprolactone.

13. Polysiloxane dispersion according to claim 1, wherein the outer phase contains polycarboxylic acid esters of bisphenol A with a mean molecular weight of 500 to 100,000.

14. Polysiloxane dispersion according to claims 1 to 13, wherein the three-dimensionally polymerizable polyorganosiloxanes are derived from siloxane units having the general formula

$$-(R_2SiO)- \qquad (1)$$

wherein the two monovalent R radicals, which may be identical or different, represent linear or ramified alkyl groups with 1 to 18 C-atoms, cycloaliphatic groups with 4 to 8 C-atoms, linear or ramified alkenyl groups with 2 to 4 C-atoms, phenyl or alkylphenyl groups with 1 to 12 C-atoms in the aliphatic radical, the hydrocarbon radicals may be substituted by halogens or hydroxyl, carboxyl, carboxylic acid anhydride, amino, epoxy, alkoxy or alkenyloxy groups, and also polyether or polyolefin groups as well as hydrogen, the groups being linked directly or via an oxygen or nitrogen atom to a silicon atom of the polysiloxane chain.

15. Polysiloxane dispersion according to claim 14, wherein the polyorganosiloxane is a block copolymer, wherein monovalent radicals R′ and R′′ are arranged in blocks alongside the main siloxane chain, derived from polymer units with the general formula

$$-(R'_2SiO)_x-(R''_2SiO)_y- \qquad (2)$$

the R' and R'' radicals that have the same significance as R being different from one another, while the R' and R'' radicals may be identical or different from one another, and x and y are equal to 1 or whole multiples thereof.

16. Polysiloxane dispersion according to claims 14 and 15, wherein at least 50% of R, R' and R'' radicals are methyl and/or phenyl groups.

17. Polysiloxane dispersion according to claims 1 to 15, wherein the polyorganosiloxane particles dispersed in the outer phase have a mean diameter of around 0.05 to 10 µm.

18. Polysiloxane dispersion according to claims 1 to 16, wherein the polyorganosiloxane particles dispersed in the outer phase have a mean diameter of around 0.07 to 5 µm.

19. Polysiloxane dispersion according to claims 1 to 16, wherein the polyorganosiloxane particles dispersed in the outer phase have a mean diameter of around 0.07 to 1 µm.

20. Process for the production of polysiloxane dispersions according to claims 1 to 19, wherein

(a) an emulsion is produced consisting of 0.1 to 75% by weight of one or several three-dimensionally polymerizable liquid polyorganosiloxanes as dispersed phase in 25 to 99.9% by weight of an outer phase consisting of monomeric or polymeric polyoles liquefying at temporatures of 20 to 100°C, linear or ramified polyglycolethers, polyesters on a polyole base, and aliphatic, cycloaliphatic or aromatic

dicarboxylic acids, aliphatic polylactones and/or polycarbonates, and 0 to 20% by weight of known accessory substances, preferably solvents, softeners, polymerizers, catalysts, stabilizers, dispersants, hardeners, reaction-mediators and/or agents to influence the viscosity of the outer phase, wherein the polyorganosiloxane droplets have a mean diameter of around 0.02 to 50 µm, and

(b) polymerization takes place in the polyorganosiloxane droplets in a known manner with formation of solid particles.

21. Process according to claim 20, wherein in step (a) 2 to 50% by weight of one or several three-dimensionally polymerizable liquid polyorganosiloxanes are used.

22. Process according to claim 20, wherein the polymerizable polyorganosiloxane or polyorganosiloxane mixture used in step (a) has an average molecular weight of 1,000 to 100,000.

23. Process according to claim 20, wherein the polymerizable polyorganosiloxane mixture used in step (a) has an average molecular weight of 1,200 to 30,000.

24. Process according to claims 20 to 23, wherein the liquid polymerizable polyorganosiloxanes are first dispersed in an initial liquid medium miscible with the actual outer phase and next the dispersion obtained is added to the actual outer phase and mixed with it, and polymerization of the

polyorganosiloxanes takes place in an appropriate manner before, during or after mixing with the actual outer phase, and optionally the first dispersion medium is removed entirely or in part after termination of mixing.

25. Process according to claims 20 to 23, wherein the liquid polymerizable polyorganosiloxanes are first dispersed in an initial liquid medium that is not miscible with the actual outer phase, the dispersion obtained is then mixed with the actual outer phase and next the first dispersion medium is removed by appropriate means entirely or in part, and polymerization of the polyorganosiloxanes is carried out before, during or after mixing with the actual outer phase, or removal of the first medium.

26. Process according to claims 24 to 25, wherein water is used as dispersant.

27. Process according to claims 20 to 26, wherein the liquid polymerizable polyorganosiloxanes are first mixed with polymerizers and/or catalysts and only then emulsified in the outer phase, conditions being so selected that transition of the polysiloxane particles from the liquid to solid state only takes place after termination of the process of emulsification.

28. Process according to claims 20 to 26, wherein appropriate polymerizers and/or catalysts are added only after formation of the polyorganosiloxane emulsion, as a result of which polymerization of the liquid polyorganosiloxane particles

takes place.

29 Use of polysiloxane dispersions according to claims 1 to 19 as preliminary products for the production of silicon-modified thermoplastic, duroplastic or elastomeric plastics on a polyurethane, polyurea, saturated polyester and polycarbonate base.